Electrolysis and recycling of CO2 into CO2-neutral fuels

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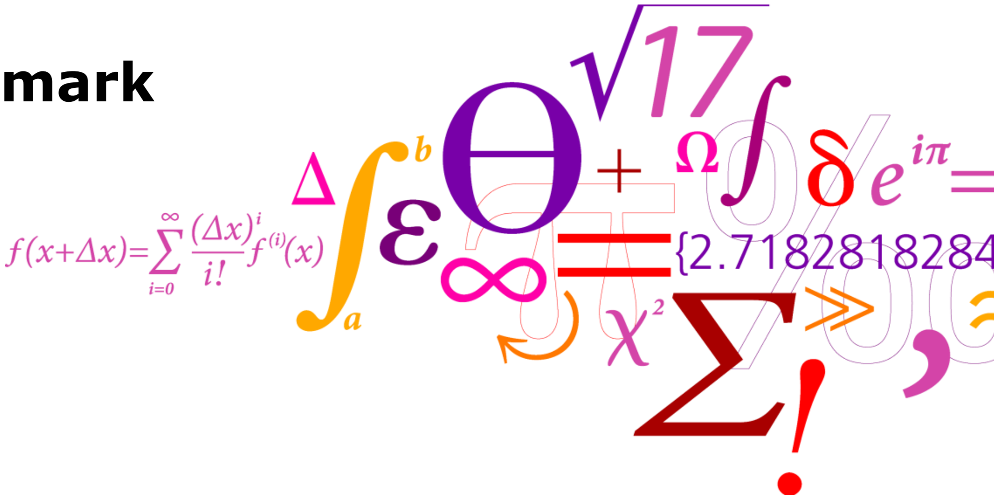

Contributing colleagues

In alphabetic order:

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Outline

1. Introduction
2. Potential availability of renewable energy
3. Electrolysis is necessary
4. Synthetic fuels via syngas
5. Motivation for synthetic hydrocarbons
6. Visions
7. Thermodynamics
8. Types and status of electrolysers
9. Haldor Topsoe Technology
10. Economy
11. Concluding remarks

Introduction

- **Wish to increase the production of sustainable and CO_2 neutral energy - "green house" effect – not enough inexpensive oil**

- **Denmark aims to become independent of fossil fuel by 2050.**

  Energy strategy 2050 - from coal, oil and gas to green energy, The Danish Government, February 2011, http://www.ens.dk/Documents/Netboghandel%20-%20publikationer/2011/Energy_Strategy_2050.pdf

- **Natural to look for photosynthesis products (biomass), but not enough biomass**

  H. Wenzel, "Breaking the biomass bottleneck of the fossil free society", Version 1, September 22nd, 2010, CONCITO, http://www.concito.info/en/udgivelser.php

Enough renewable energy?

- **Yes, fortunately, enough is potentially available.**

- **The annual global influx from sun is ca. 3 - 4·10^{24} J - marketed energy consumption is ca. 5·10^{20} J;**

  1)A. Evans et al., in: Proc. Photovoltaics 2010, H. Tanaka, K. Yamashita, Eds., p. 109.

  2) Earth's energy budget, Wikipedia, http://en.wikipedia.org/wiki/Earth's_energy_budget.

  3) International Energy Outlook 2010, DOE/EIA-0484(2010), U.S. Energy Information Administration, http://www.eia.gov/oiaf/ieo/index.html

- **Earth's surface receives at least ca. 6 - 8,000 times more energy than we need. In deserts, intensity is higher than average at the same latitude – dry air**

Area needed

- If 0.2 % of the earth's area (ca. 1 mill. km^2 or 15 % of Australia) and if collection efficiency = 10 %, we get enough energy.

- Besides solar we also have geothermal and nuclear (fusion and fission) potential energy sources.

- CO_2 free nuclear - more efficient if affordable storage technology is available.

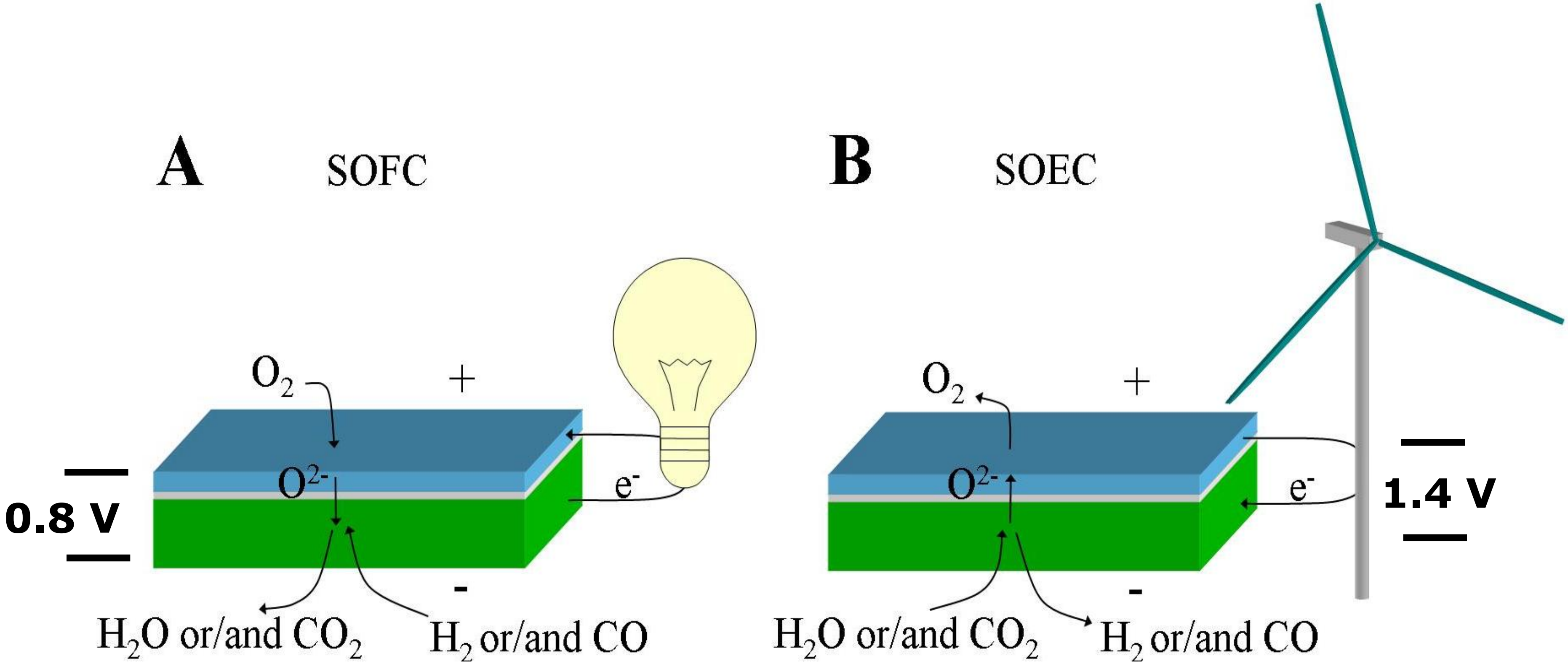
- Important part of the solar energy is actually converted to biomass, hydro and wind energy – easier to harvest.

We need electrolysis

- **Many technical principles are pointed out as suitable for storage technologies:**
  - **pumping of water to high altitudes**
  - **batteries**
  - **superconductor coil (magnetic storage)**
  - **flywheels**
  - **Thermo-chemical looping**
  - **Solar Thermal Electrochemical**
  - **Photo-electrochemical HER and CO_2 reduction**
- **All are very important! But: first 4 are not for long distance (> 500 km) transport. 3 last are early stage research - may prove efficient in the future.**

- **Therefore, within a foreseeable future: Electrolysis is necessary in order to get enough renewable fuels!**

Principle of electrolysis (SOC)



850 °C EMF ca. 1.1 V

Working principle of a reversible Solid Oxide Cell (SOC). The cell can be operated as a SOFC (A) and as a SOEC (B).

Production of syngas (SOEC case)

Reaction Schemes:

The overall reaction for the electrolysis of steam plus CO_2 is:

$$H_2O + CO_2 + \text{heat} + \text{electricity} \rightarrow H_2 + CO + O_2 \qquad (1)$$

This is composed of three partial reactions. At the negative electrode:

$$H_2O + 2e^- \rightarrow H_2 + O^{2-} \qquad (2)$$

$$CO_2 + 2e^- \rightarrow CO + O^{2-} \qquad (3)$$

and at the positive electrode:

$$2\,O^{2-} \rightarrow O_2 + 4e^- \qquad (4)$$

Production of syngas from H_2 and CO_2

The water-gas shift (WGS) reaction:

$$CO_2 + 2\ H_2 \leftrightarrows CO + H_2 + H_2O$$

By condensation of the water pure syngas is obtained

Methane synthesis

If H_2 only is produced by low temperature electrolysis:

- **$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$ Sabatier reaction**

or

- **make syngas from CO_2 by shift reaction and then:**

- **$CO + 3\ H_2 \leftrightarrows CH_4 + H_2O$**
- **Ni - based catalysts,**
- **190 °C – 450 °C**
- **3 MPa, i.e. pressurized**
- **in principle possible to produce inside SOEC stack on Ni-electrode, but CH_4 not stable at 650 °C +**

Methanol and DME synthesis

- **$CO + 2\ H_2 \leftrightarrows CH_3OH$**
- **$2\ CO + 4\ H_2 \leftrightarrows (CH_3)_2O + H_2O$**
- **A $Cu/ZnO\text{-}Al_2O_3$ catalyst**
- **200 °C - 300 °C**
- **4.5 - 6 MPa, again the electrolyser should be pressurized**

Why synthetic hydrocarbons? The energy density argument

Type	MJ/l	MJ/kg	Boiling point °C
Gasoline	33	47	40 - 200
Dimethyl ether - DME	22	30	- 25
Liquid hydrogen	(10)	(141)	-253
Water at 100 m elevation	10^{-3}	10^{-3}	
Lead acid batteries	0.4	0.15	
Li-ion batteries	1	0.5	

Why synthetic fuel? The power density argument

- **Gasoline filling rate of 20 L/min equivalents <u>11 MW</u> of power and means it takes 2½ min to get 50 l = 1650 MJ on board**

- **For comparison: Li-batteries usually requires 8 h to get recharged. For a 300 kg battery package (0.5 MJ/kg) this means a power of ca. 3.5 kW i.e. it takes 8 h to get 150 MJ on board.**

- **The ratio between their driving ranges is only ca. 5, because the battery-electric-engine has an efficiency of ca. 70 % - the gasoline engine has ca. 25 %.**

Visions for synfuels from electrolysis of steam and carbon dioxide

1. **Big off-shore wind turbine parks coupled to a large SOEC – produce CH_4 (synthetic natural gas, SNG) - feed into existing natural gas net-work (in Denmark).**

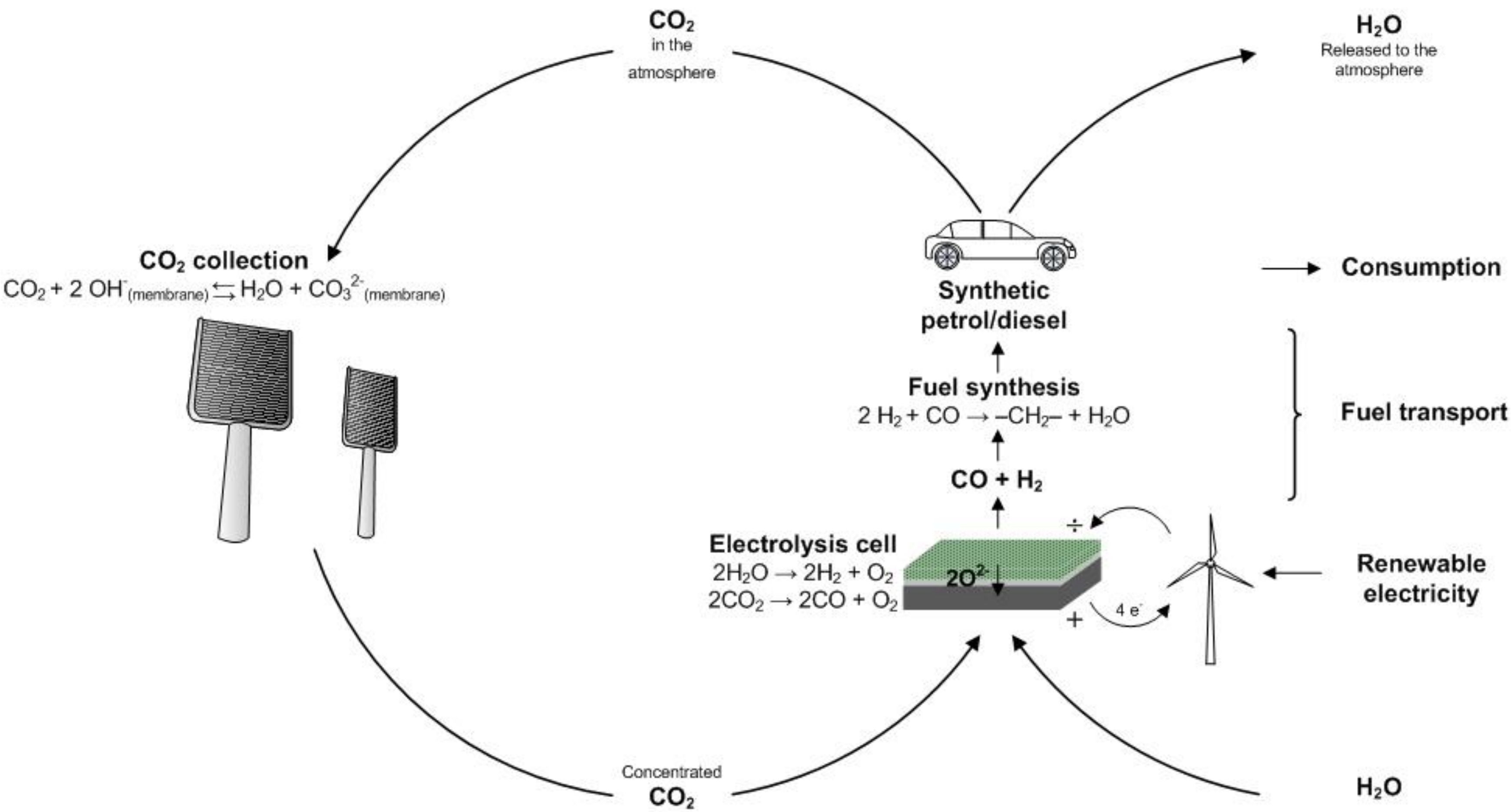
2. **Large SOEC systems - produce DME, gasoline and diesel - Island, Canada, Greenland, Argentina, Australia ... geothermal, hydro, solar and wind.**

3. **Target market: replacement of natural gas and <u>liquid fuels for transportation</u>**

4. **All the infrastructure exists!!**

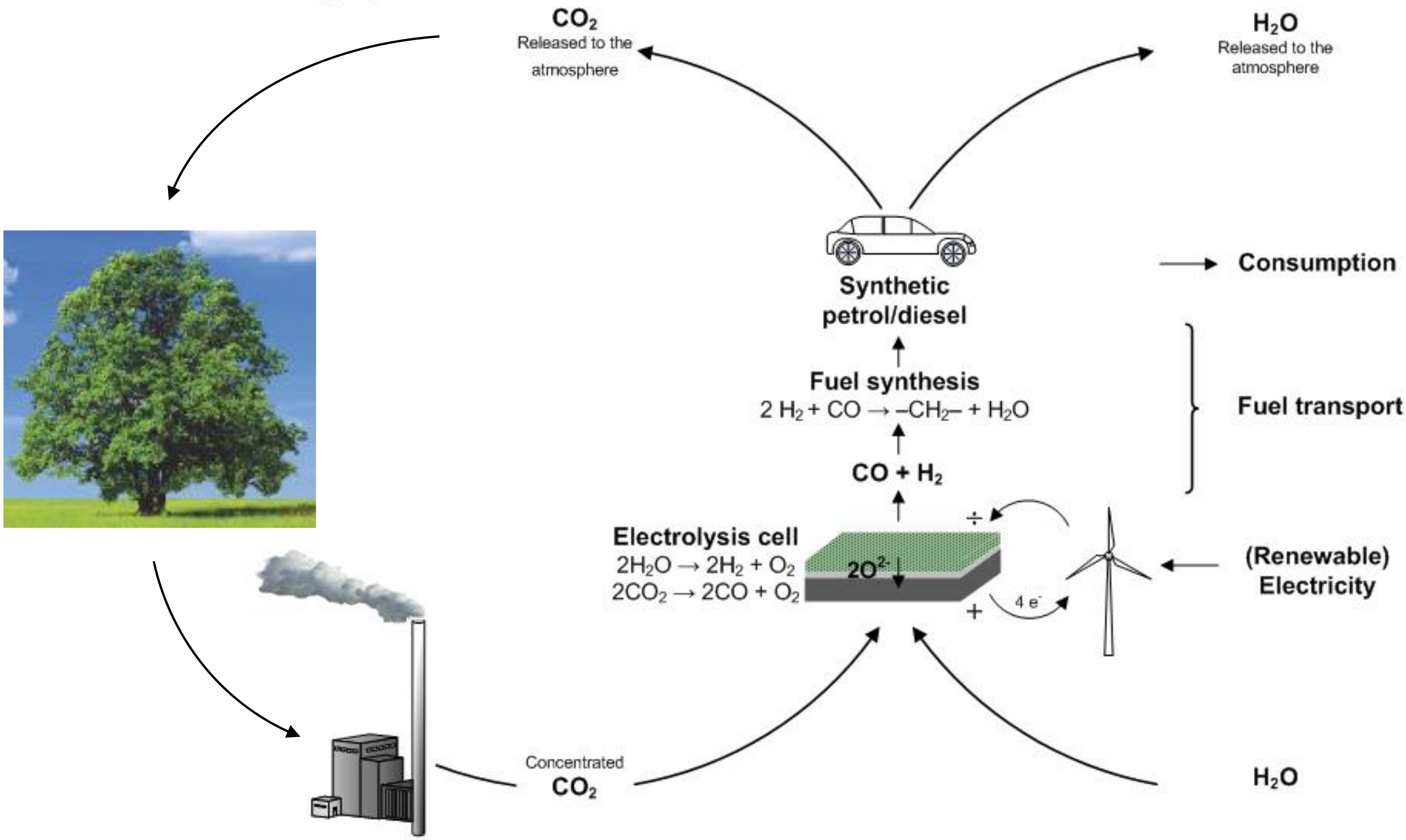
Vision, co-electrolysis for transport fuels

Long term realisation - CO_2 capture from the atmosphere



Vision, Biomass CO_2 recycling

Short term realisation - CO_2 capture from industrial sources



First conclusion

There is probably a need for all kinds of energy conversion and storage technologies in the future, but:

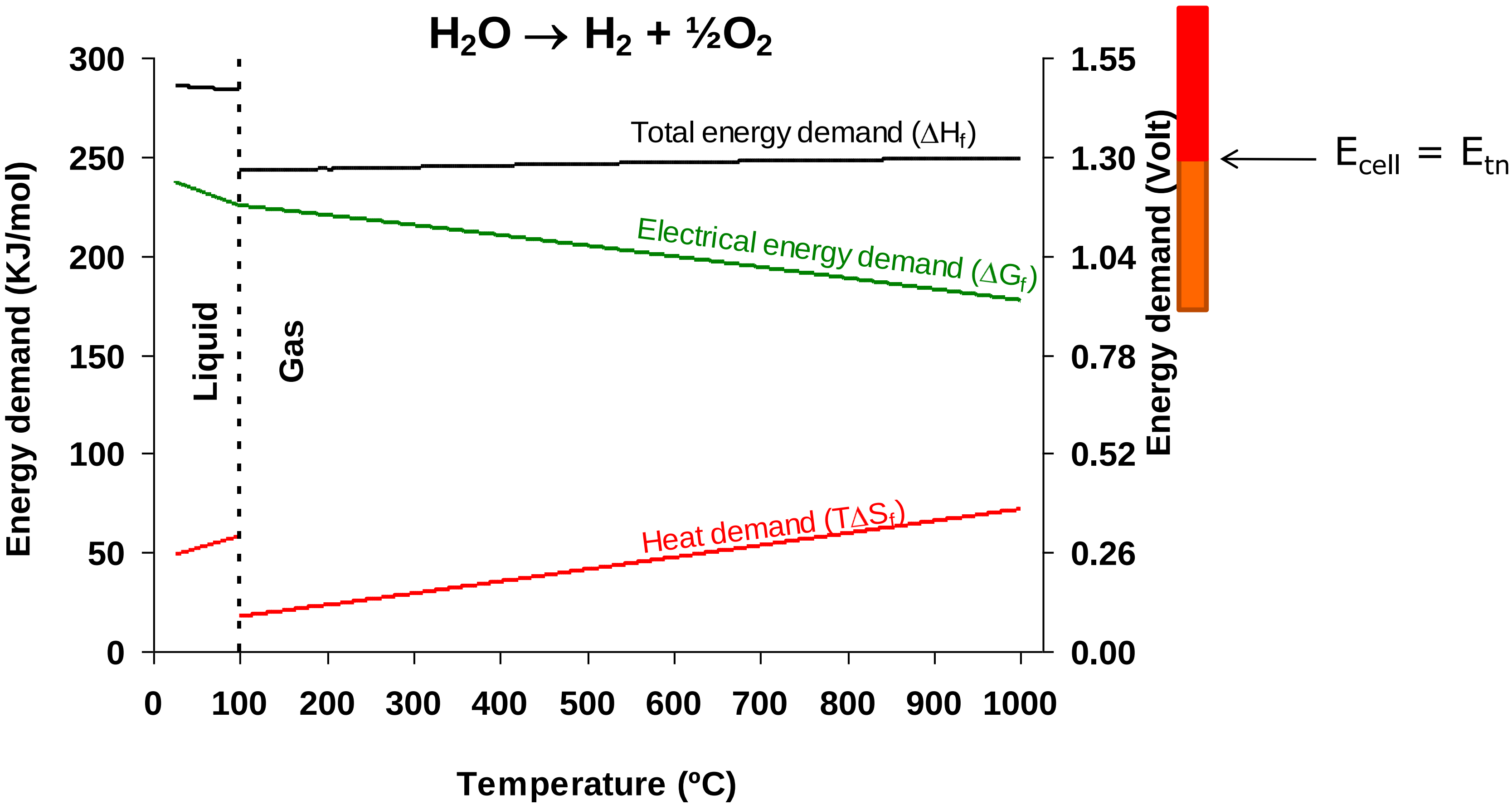
<u>Electrolyser combined with catalytic reactor for liquid hydrocarbons and CH_4 (SNG) is the type we need the most</u>

Preferably, the electrolysers cells should be reversible – i.e. the very same stack should be able to operate in fuel cell mode using the synthetic fuel

☺

So, which electrolyzer options do we have?

Thermodynamics



Energy ("volt") = Energy (kJ/mol)/2F

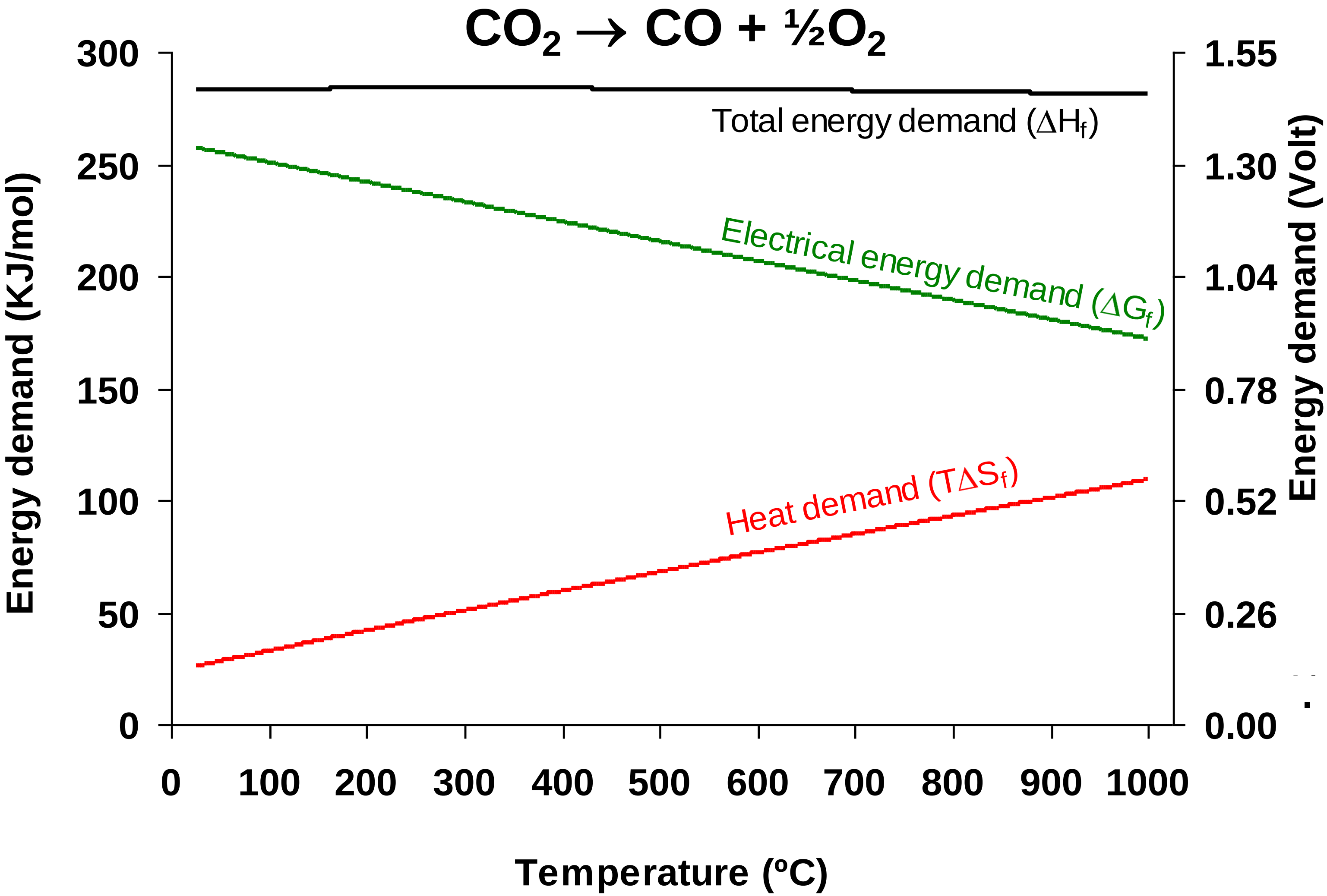
$E_{tn} = \Delta H/2F$

$i \propto E_{cell} - \Delta G/2F$

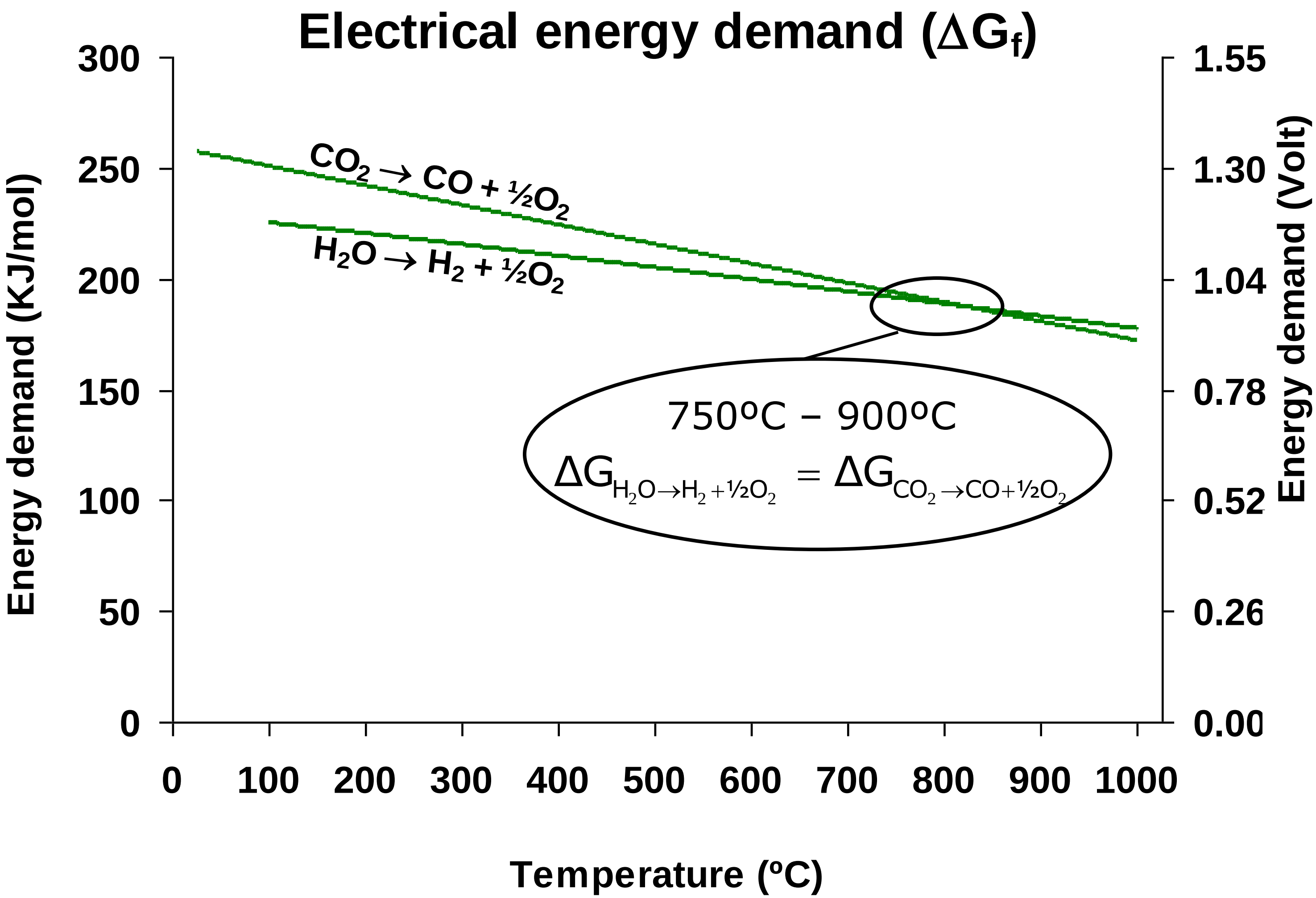
Price $\propto$ 1/i [A/cm²] ,

$\Delta H/\Delta G > 1$, $\eta = 100\ \%$ at $E = E_{tn}$ (no heat loss)

Thermodynamics



Thermodynamics: CO_2 and H_2O



Electrolysis Cell Types

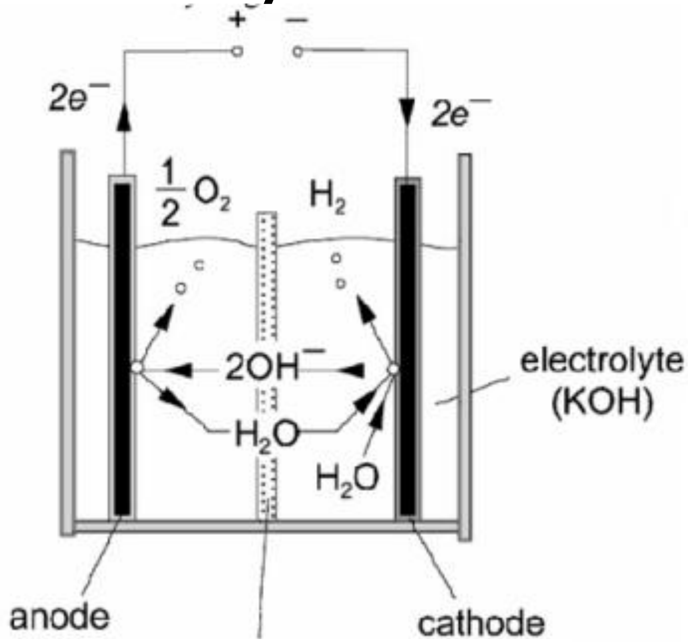
1. **Simple aqueous electrolytes (e.g. KOH or K_2CO_3), room temperature to ca. 100 °C, 0.1 - 3 MPa pressure**
2. **Low temperature "solid" proton conductor membrane (PEM), 70 – 90 °C, and high temperature PEM 120 - 190 °C.**
3. **Immobilized aqueous K_2CO_3, Na_2CO_3 etc. in mesoporous structures – pressurized 200 – 300 °C, 0.3 – 10 MPa**
4. **Solid acids, 200 – 250 °C, pressurized?**
5. **Molten carbonate electrolytes, 800 – 950 °C, 0.1 MPa**
6. **High temperature solid oxide ion conductor (stabilized zirconia), 650 – 950 °C, pressurized 0.5 – 5 MPa**

Electrolyzer status

- **Few types commercialized but - from an energy conversion and storage point of view - none of them are commercial in today's energy markets.**
- **The classical alkaline electrolyser was commercialized during the first half of the 20th century.**
- **If significant amounts of synfuel via electrolysis in the very near future (the next 1 -5 years) – only alkaline electrolysers is available on some scale.**

Principle of Alkaline Electrolysis cell (AEC)

Electricity + Heat → **Chemical energy**



Separator

Anode: $4\ OH^- \rightarrow O_2 + 2\ H_2O + 4\ e^-$

Cathode: $2\ H_2O + 4\ e^- \rightarrow 2H_2 + 4\ OH^-$

Total: $2\ H_2O \rightarrow 2\ H_2 + O_2$

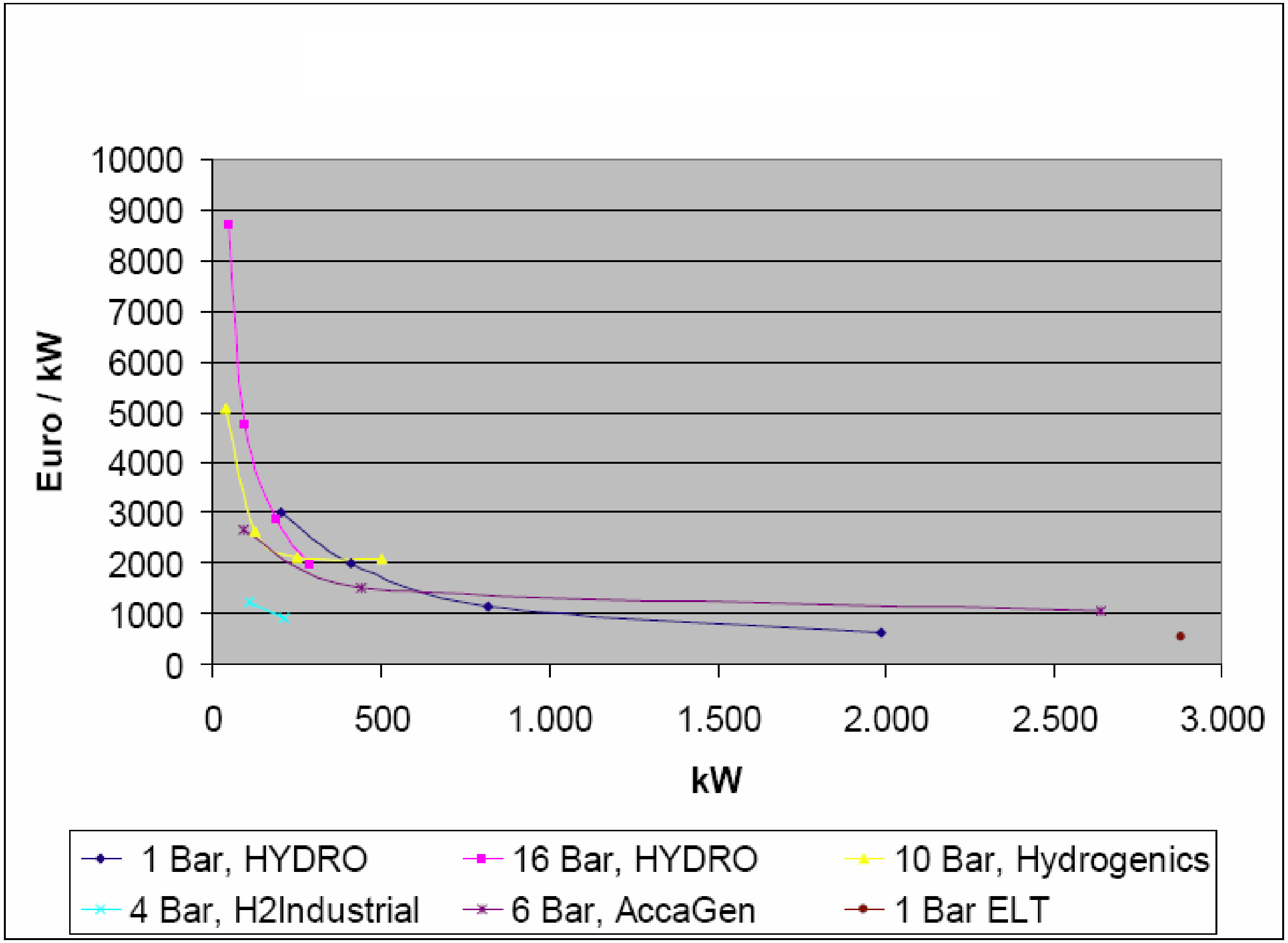
Produces only Hydrogen – further reactions are necessary in order to produce hydrocarbon fuels

High costs due to low current density or low efficiency

Aqueous electrolyte

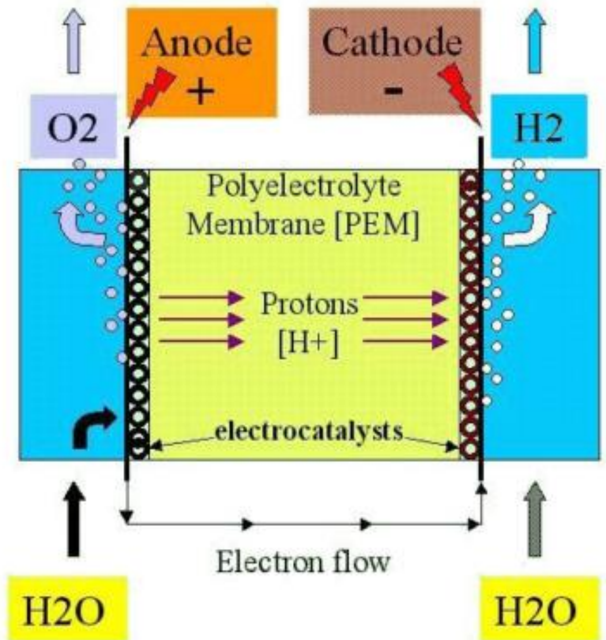
KOH in water	**Ni or Ni/Co-oxides**	**Ni on steel**	**80 °C**	**Low temp: LT-AEC**

Price of LT-AEC



Ref.: J.O. Jensen, V. Bandur, N.J. Bjerrum, S.H. Jensen, S. Ebbesen, M. Mogensen, N. Tophøj, L.Yde, "Pre-investigation of water electrolysis", PSO-F&U 2006-1-6287", project 6287 PSO, 2006, p. 134. http://130.226.56.153/rispubl/NEI/NEI-DK-5057.pdf

Electrolysis, principle of PEM



$$\text{Anode}: 2H_2O \rightarrow 4H^+ + O_2 + 4e^-$$

$$\text{Cathode}: 4H^+ + 4e^- \rightarrow 2H_2$$

$$\text{Cell}: 2H_2O \rightarrow 2H_2 + O_2$$

Polymer electrolyte

Very expensive!

	Electrolyte	Oxygen electrode	H_2 electrode	Auxiliary mat.	Temp.
LT-PEM	**Fluoropolymer+ SO_3H, Nafion®**	**IrO_2**	**Pt**	**Ti**	**80 °C**
HT-PEM	PFSA (Aquivion®) with H_3PO_4	**IrO_2**	**Pt**	**Ta coated steel**	**150 °C**

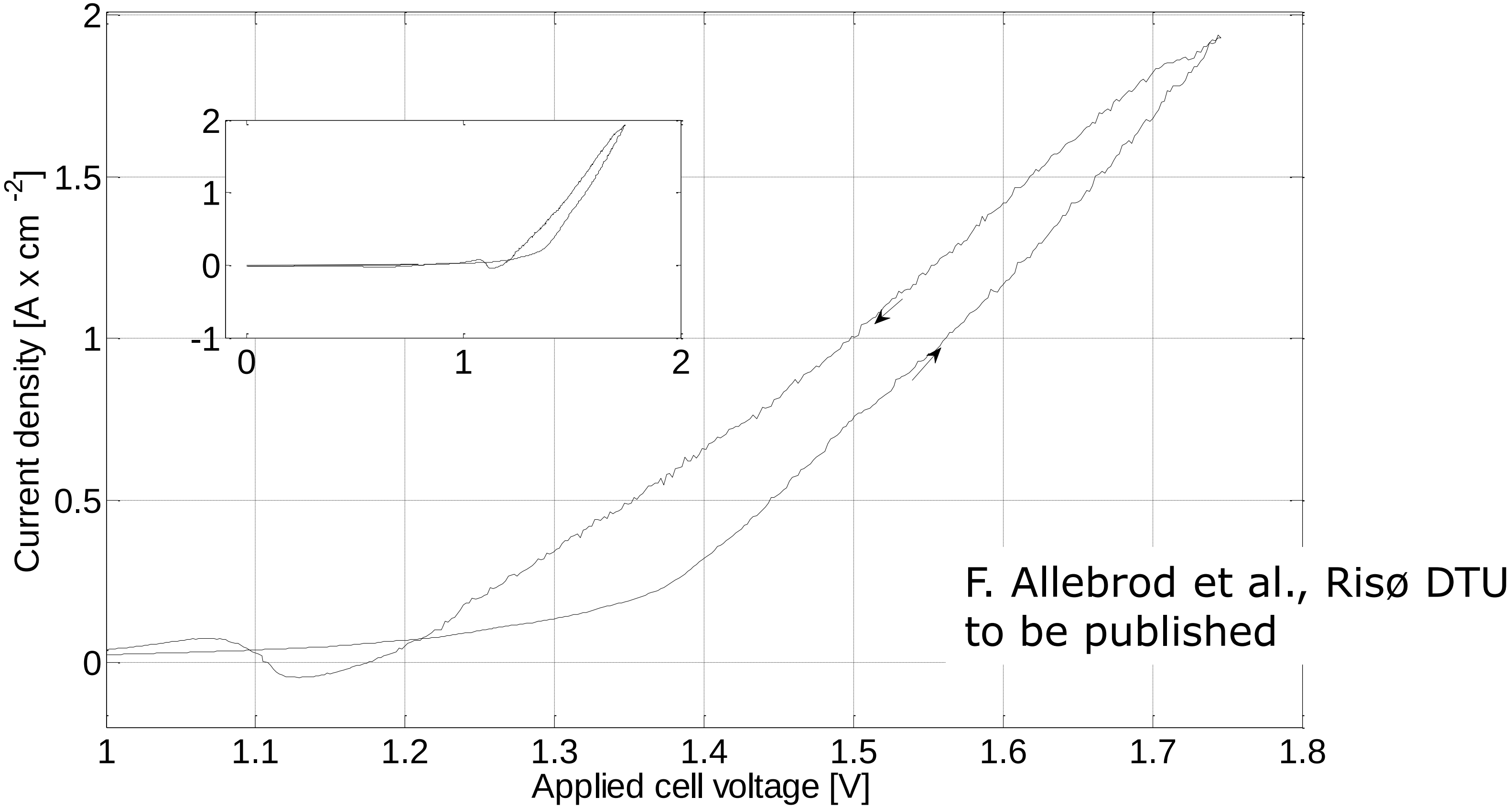
Other new 200 – 300 °C cell types

As part of the initiative called Catalysis for Sustainable Energy (CASE, www.case.dtu.dk) other types of electrolysis cells are being researched and developed at DTU.

- Solid Acids (CsH_2PO_4)
- Immobilized aqueous K_2CO_3
- Immobilized aqueous KOH

High Temperature and Pressure Alkaline (HT-AEC)

Conductivity of aqueous 45 wt% KOH immobilized in nano-porous structure reached 0.84 S·cm^{-1} at 200 ºC



Cyclic voltage sweep on a cell with nickel-based gas diffusion electrodes. Current densities of 1.0 A·cm^{-2} at 1.5V and 1.9 A·cm^{-2} at 1.75V. 3.7 MPa and 241 ºC. Calculated EMF 1.2 V. 1 cm^{2} button cell.

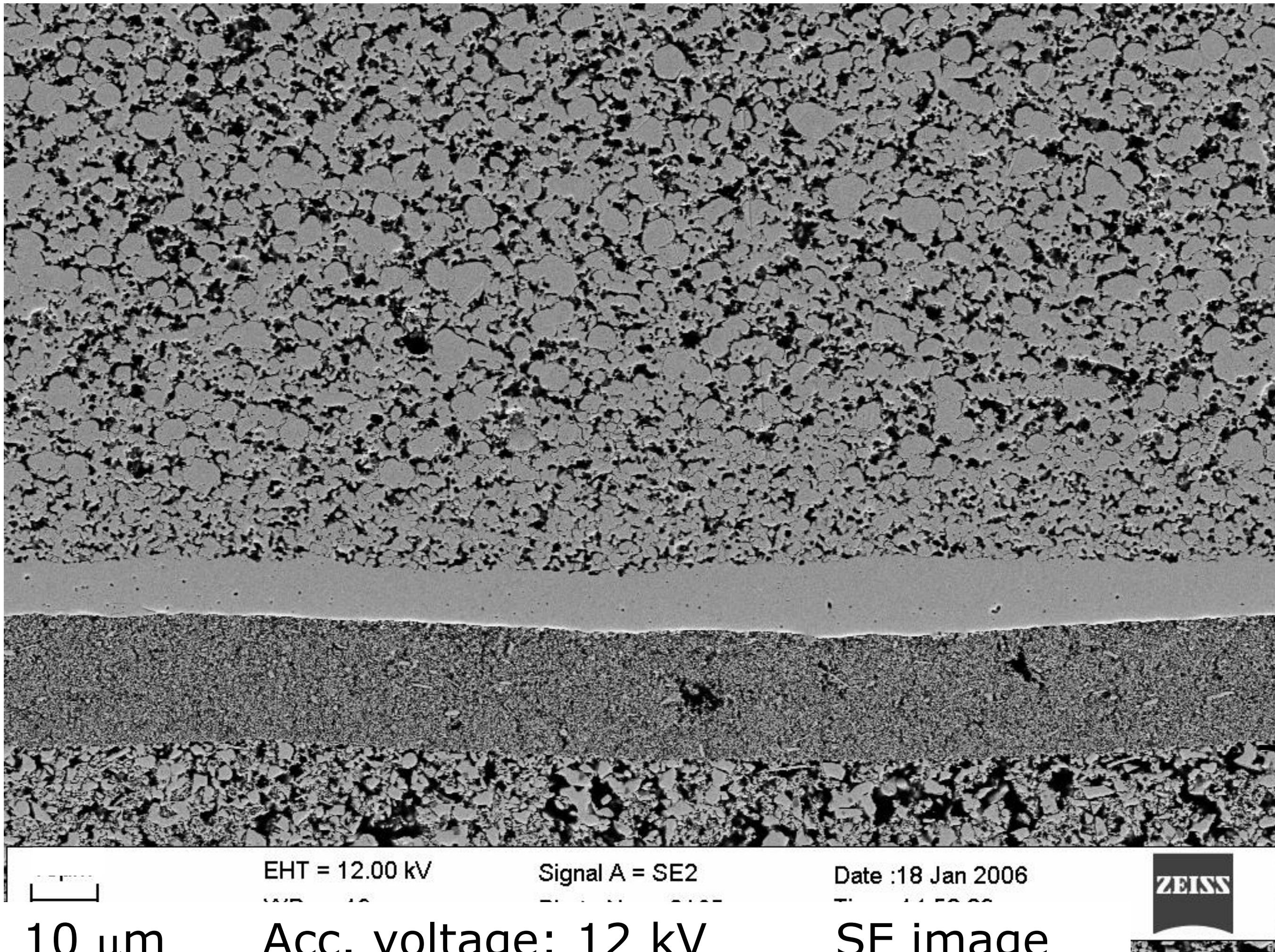
More about SOC

A solid oxide cell is an electrochemical cell, which can:

1. **Convert H_2O + CO_2 and <u>electric energy</u> into O_2 (at the + pole) and <u>H_2 + CO (syngas)</u> - may be turned catalytically into e.g. CH_3OH – SOEC**

2. **Convert O_2 (from air) and <u>energy rich gases</u> (e.g. hydrocarbons or ammonia) into <u>electric energy</u> - produces electric power - SOFC**

Ni-YSZ supported SOC



Ni/YSZ support

Ni/YSZ electrode

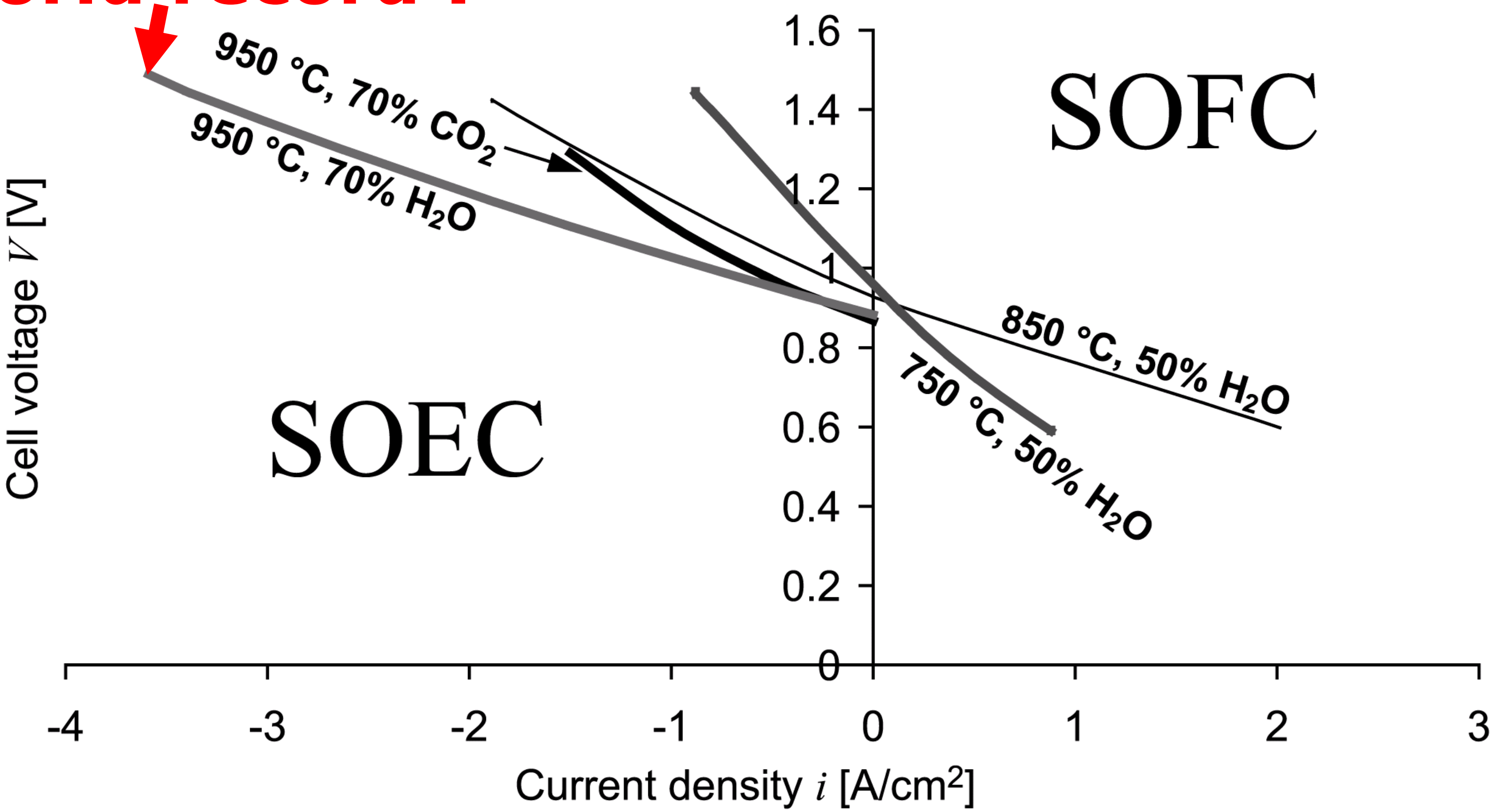
YSZ electrolyte

LSM-YSZ electrode

10 μm   Acc. voltage: 12 kV   SE image

Cell performance

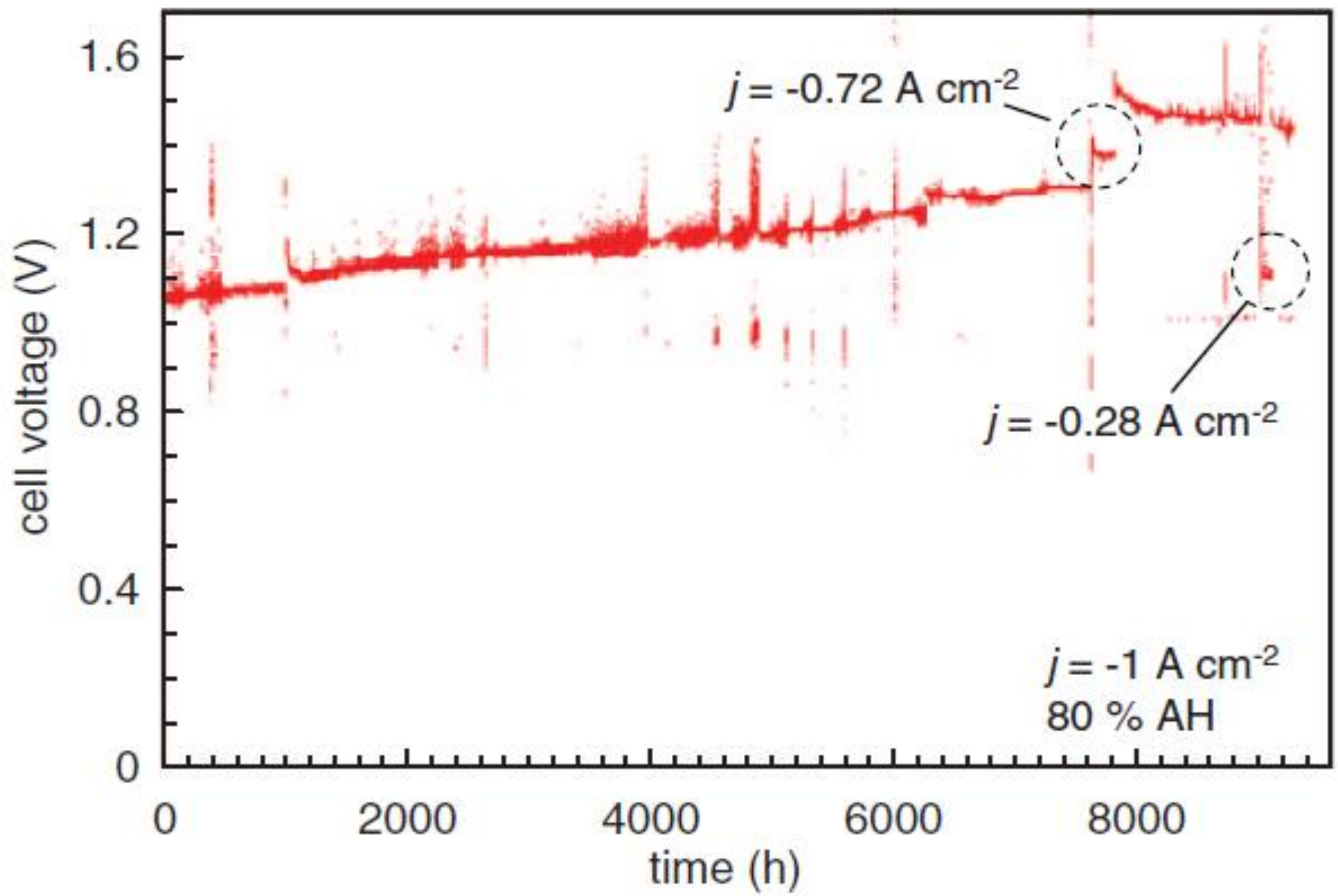
World record !



i - V **curves for a Ni-YSZ-supported Ni/YSZ/LSM SOC: electrolyzer (negative cd) and fuel cell (positive cd) at different temperatures and steam or CO_2 partial pressures - balance is H_2 or CO.**

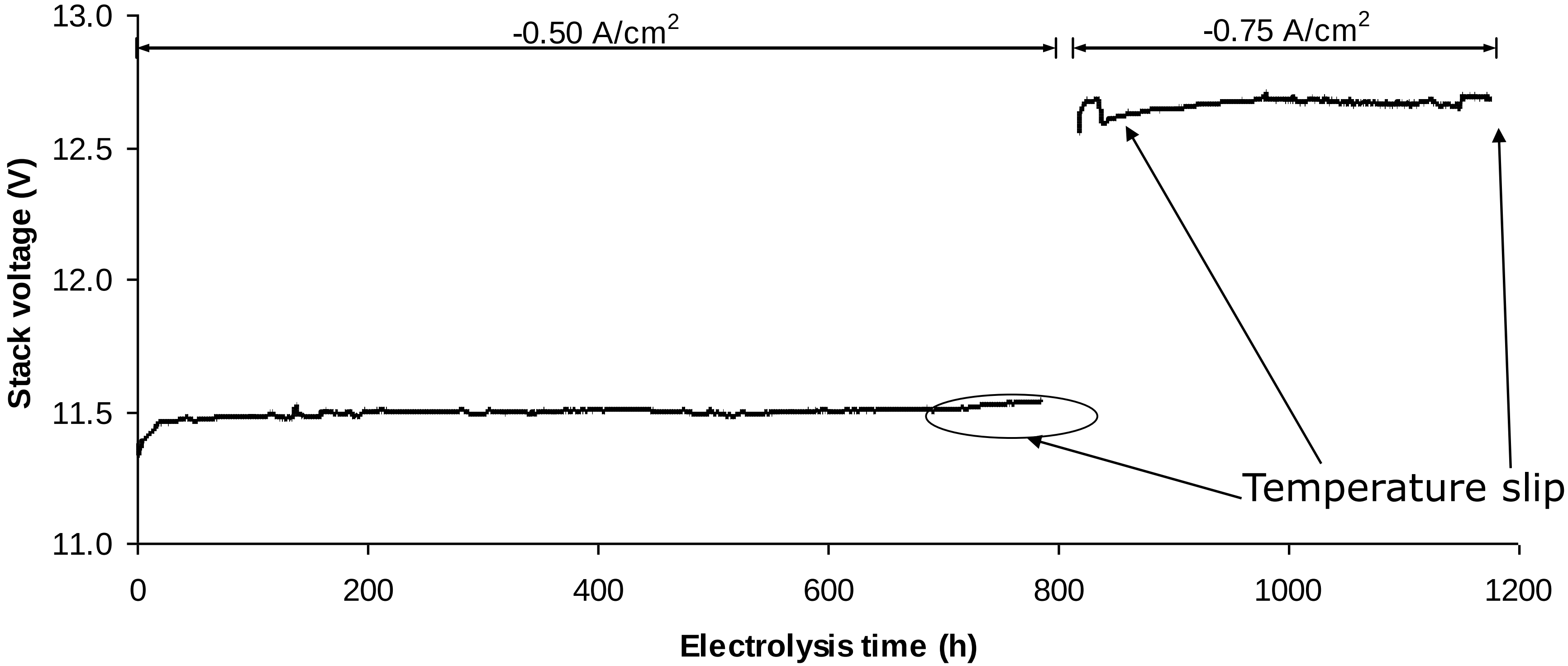
S.H. Jensen et al., International Journal of Hydrogen Energy, **32** (2007) 3253

9000 h of Operation of SOC – Steam Electrolysis



Time evolution of the cell voltage during operation with a nominal j = −1.0 A cm^{-2} (longer periods of low current density marked with circles). 45 cm^2, 780 °C. EIfER test of FZ-J single cell.
J. Schefold et al., *J. Electrochem. Soc.*, **159** (2012) A137

1 kW - 10-cell Topsoe stack – 12×12 cm², Risø DTU test

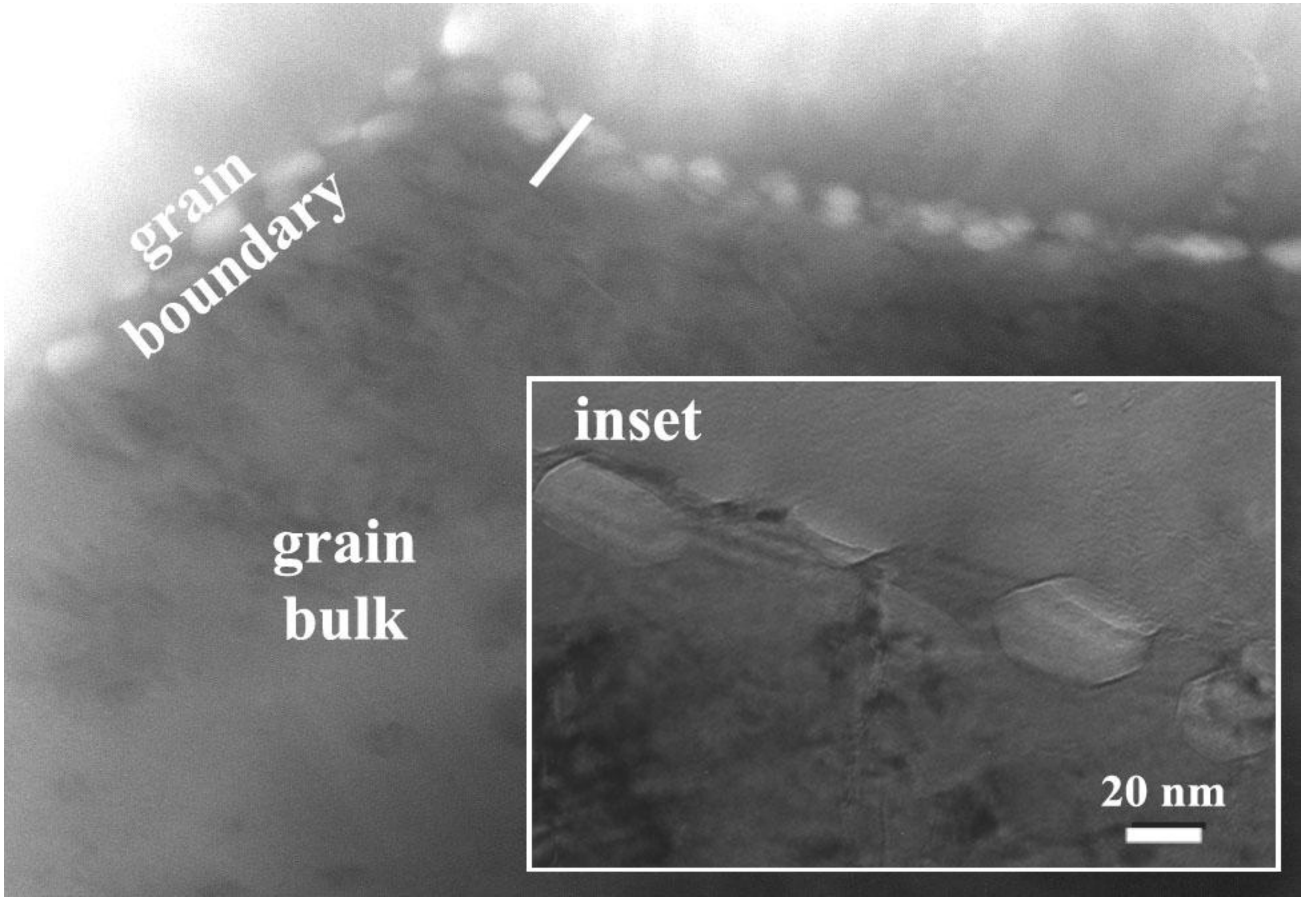


850 °C, -0.50 A/cm² or -0.75 A/cm², 45 % CO² / 45% H_2O / 10 % H_2, cleaned gases.

S. Ebbesen et al., Int. J. Hydrogen Energy, **36**, (2011) 7363

Fast degradation > ca. 1 A cm^{-2}

- 850 °C, single cell, steam, -2 A cm^{-2} for 188 h
- Electrolyte conductivity degradation - near oxygen electrode
- TEM reveals that it is due to O_2 bubble precipitation inside the electrolyte near the O_2 LSM/YSZ-electrode destroying $\sigma_{O^{2-}}$



Ruth Knibbe et al., J. Electrochem. Soc., **157** (2010) B1209

Benefits of pressure

- **Deliver gasses at pressure down stream**

- **SOEC**

  Pressurization via heat

  Reduce overpotentials (Reduce price)

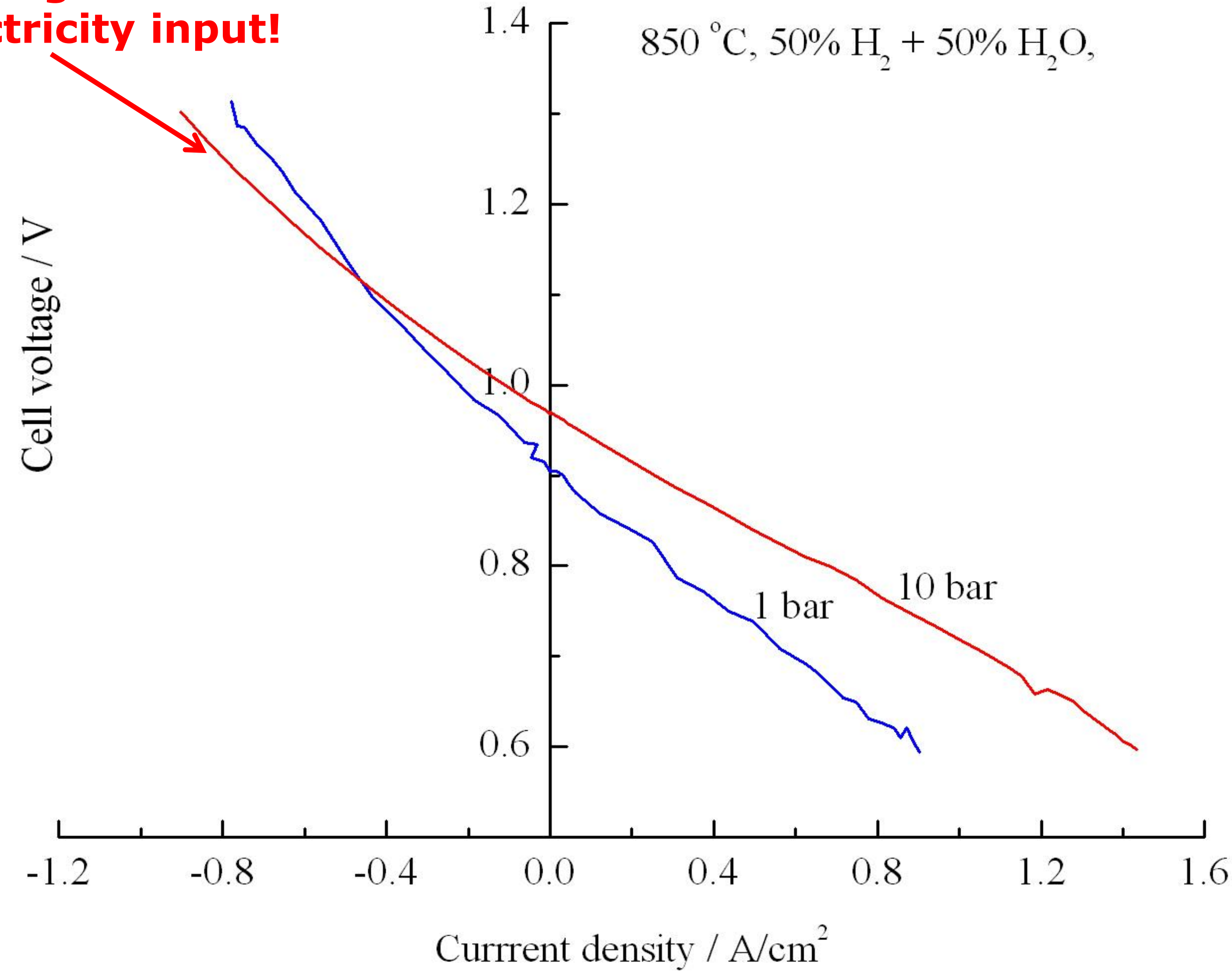
- **AEC, PEM**

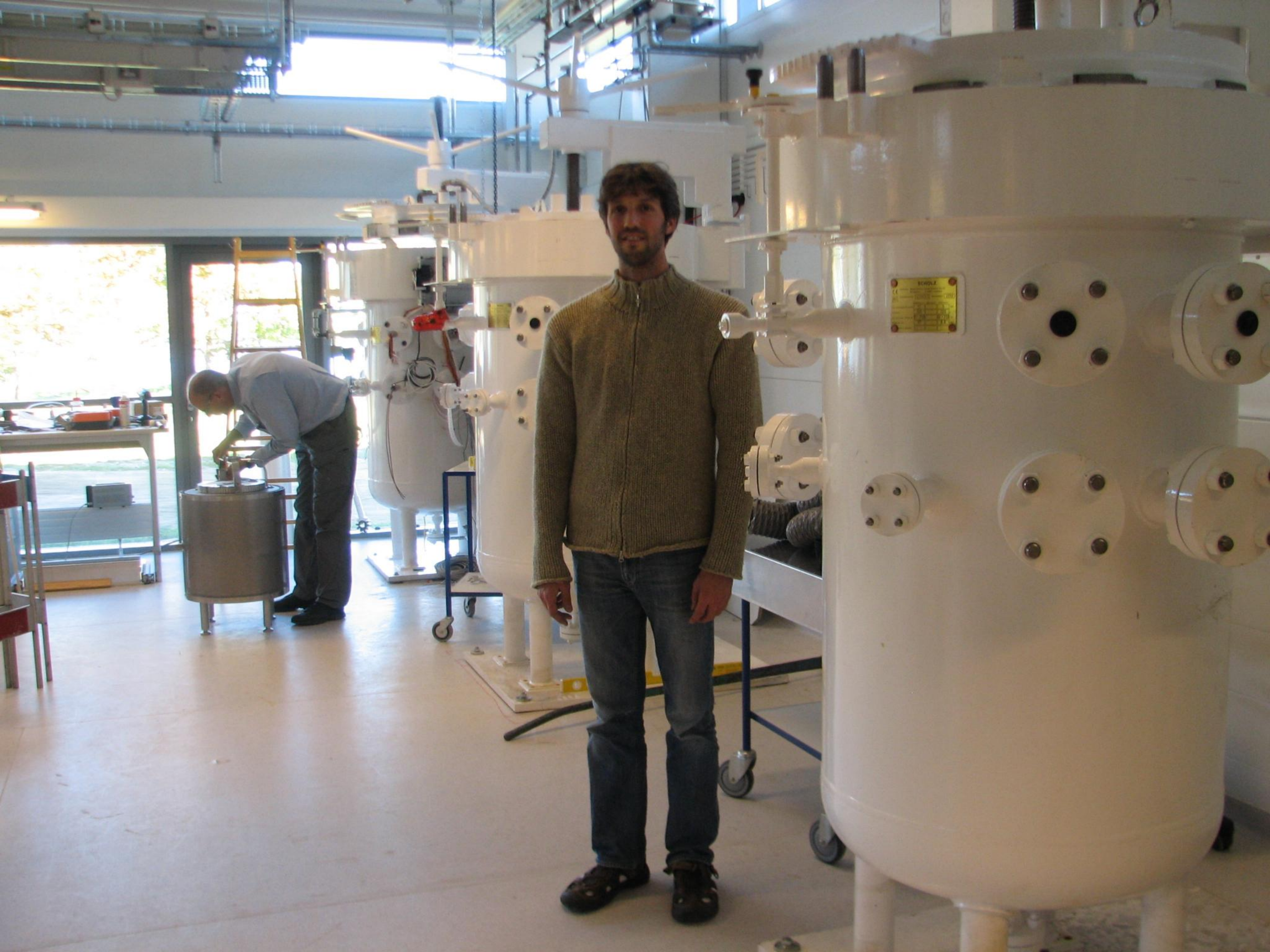
  Pressurization via electrochemistry

  Reduce overpotentials (Reduce price)

Some early results

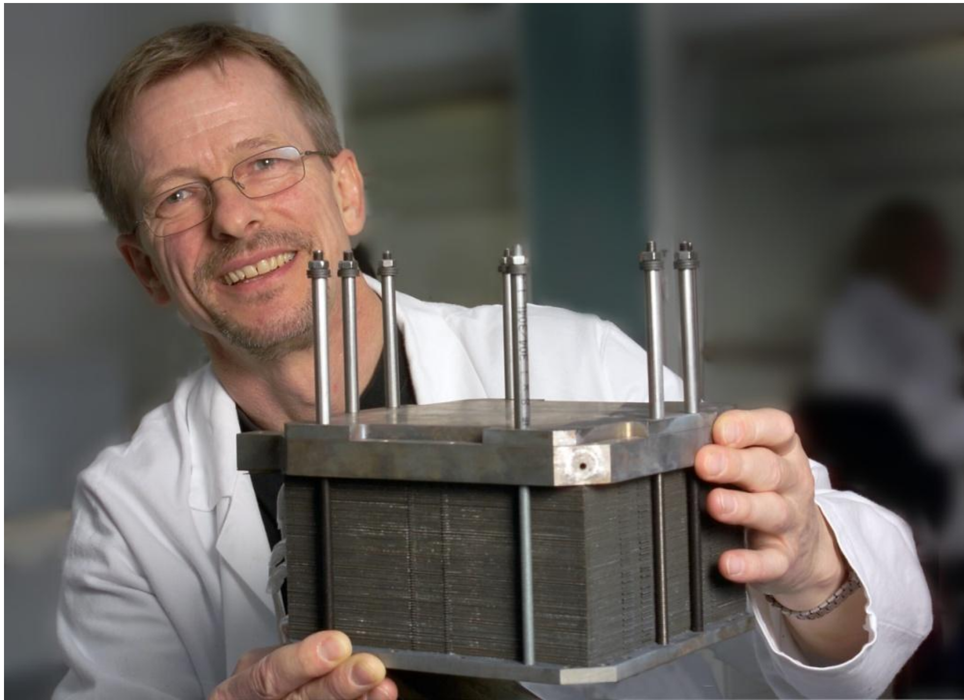
We get pressurized hydrogen with lower electricity input!





Cells stacks

- **To operate at useful voltages several cells, e.g. 50, are stacked in series**
- **High energy density: Stack electric power density of ~3 kW/liter demonstrated with Topsoe cell stacks in electrolysis mode**
- **Scalable technology: From kW to MW**



Danish SOC consortium

- **Risø DTU, Haldor Topsoe A/S and Topsoe Fuel Cell A/S have close cooperation around solid oxide cell technology.**

- **Topsoe Fuel Cell has a pilot production line for SOC. Haldor Topsøe has a industrial catalyst production and extensive know-how on fuel production from syngas.**

- **The following slides are about Haldor Topsøe A/S Syngas Technology and “green” projects**

Topsoe SynGas Technologies

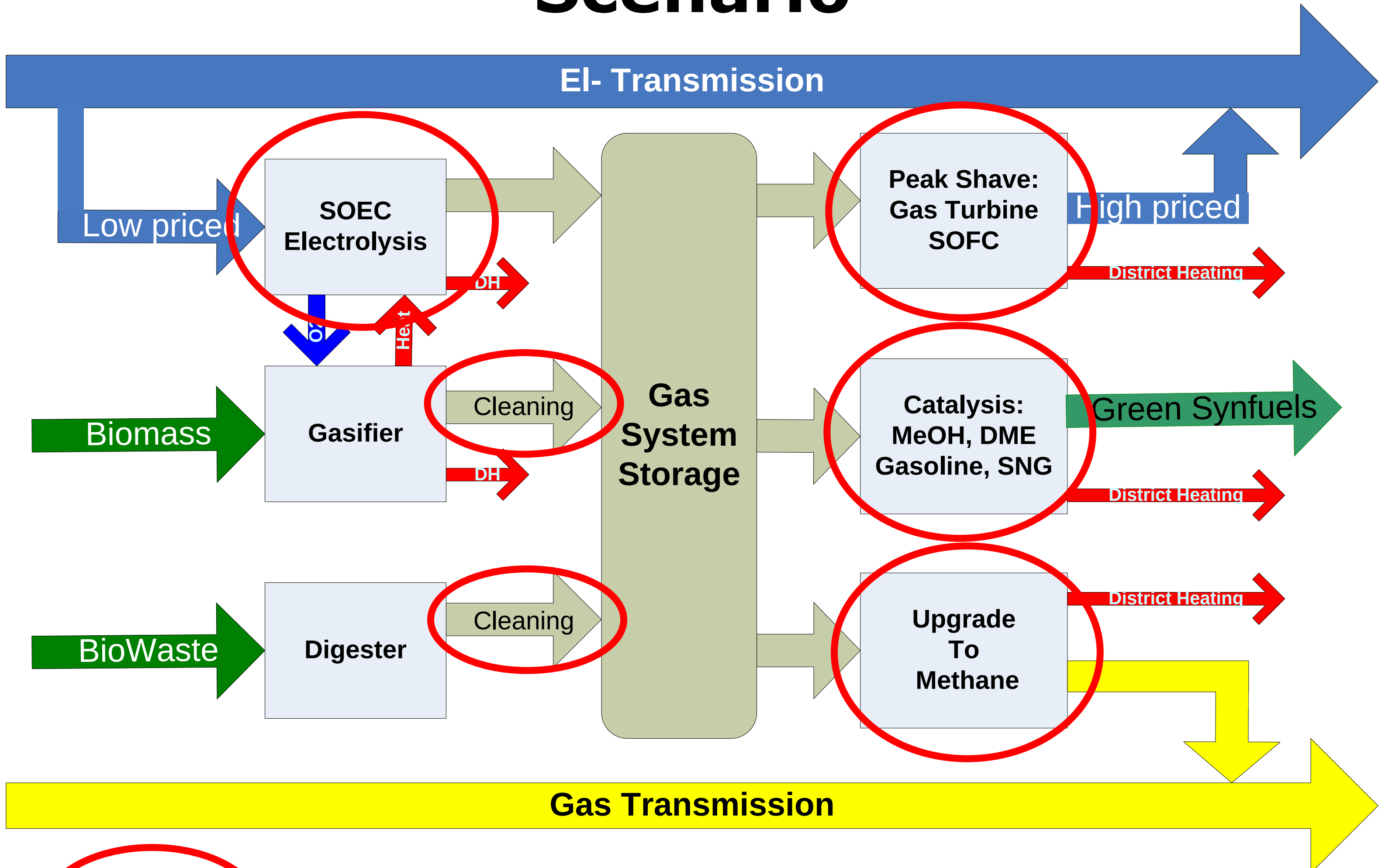
- Synthesis Gas
- Ammonia
- Hydrogen
- Carbon Monoxide
- SNG
- Methanol
- DME
- Gasoline - TIGAS

New SOFC production facility Topsoe Fuel Cell A/S

- Inauguration: April 2009
- Capacity ≈ 5 MW/yr
- Investment: >13 mio. EUR

Advanced technology – industrial relevance – low production cost

Energinet.dk's vision for fossil fuel free Denmark in 2050 – The Wind Scenario



= Topsøe Technology

Biogas upgrade by means of SOEC ForskNG Project 10677

$$CH_4 + CO_2 + 3H_2O + El \rightarrow 2CH_4 + H_2O + 2O_2$$

Participants:

Haldor Topsøe A/S

Ea Energianalyse

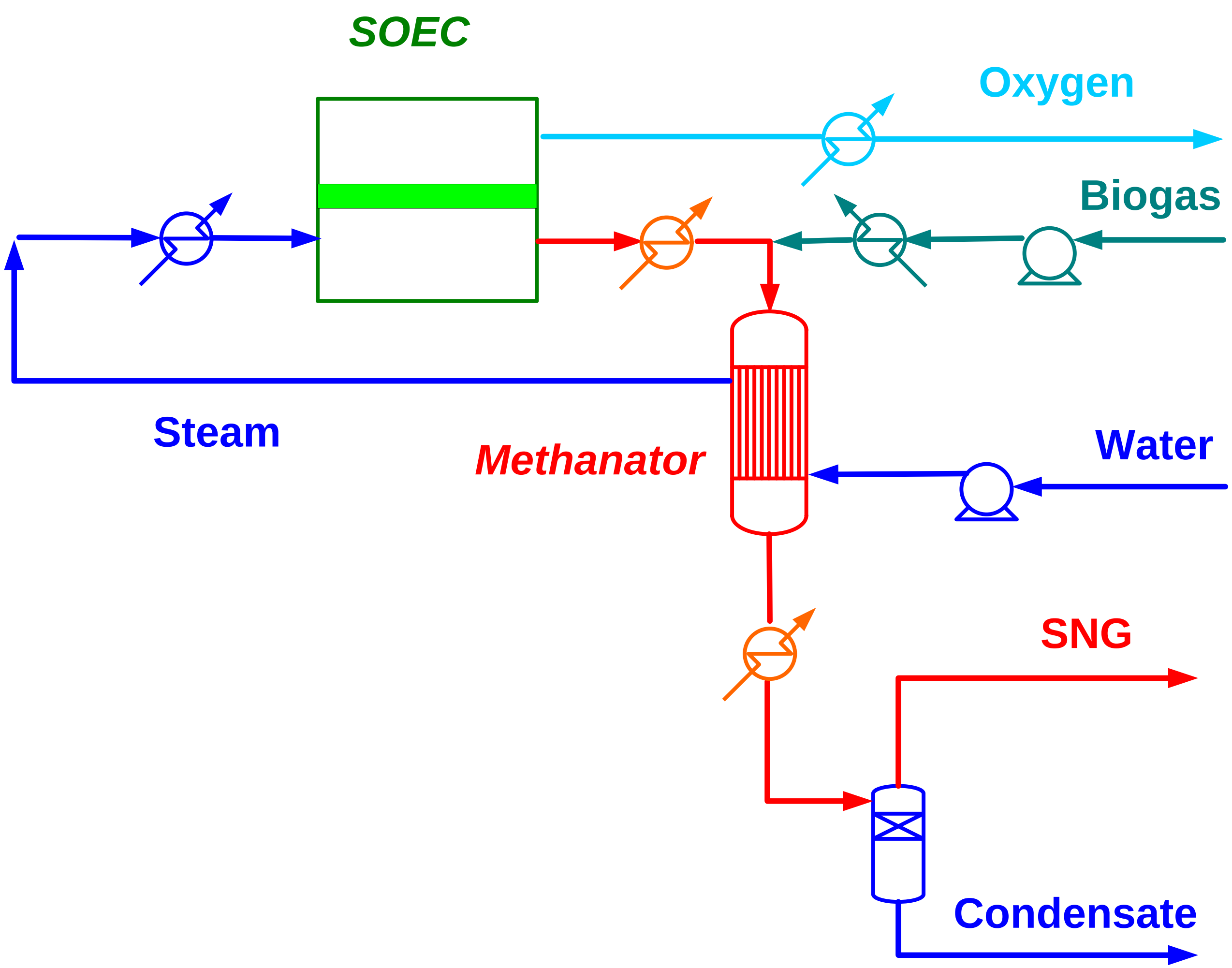
Risø DTU

Topsoe Fuel Cell A/S

ForskNG Support

911 kKr.

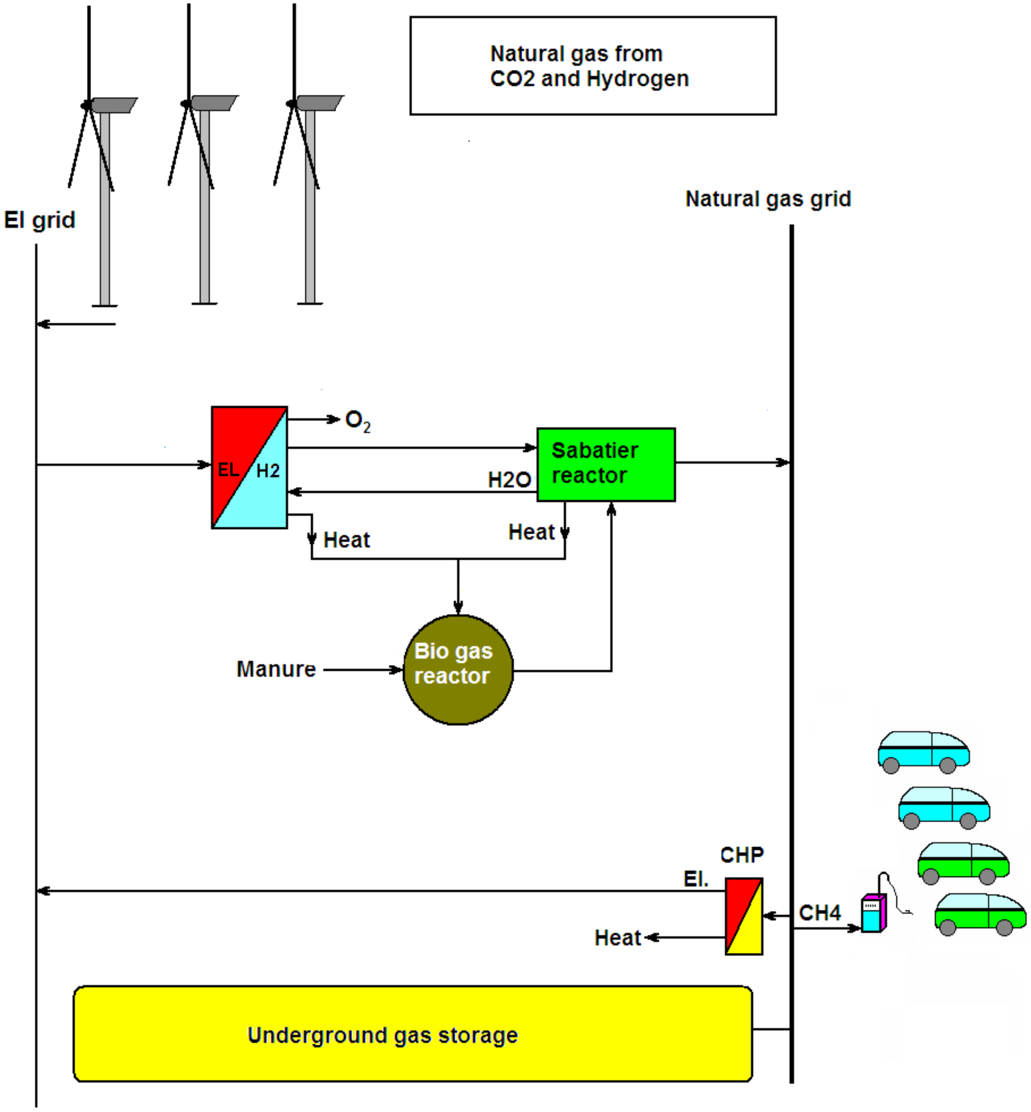
Biogas to SNG via SOEC and methanation of the CO_2 in the biogas



Biogas upgrading
Pre-project sponsored by

Planning of demo

Experimental verification of Biogas cleaning



Key numbers per year Denmark (2008)

- **Total energy consumption: 673 PJ**
- **Biogas potential: 40 PJ**
- **If upgraded by SOEC: 67 PJ ~ 10 %**
- **NG used for power plants: 73 PJ**
- **NG used in household, industry and service: 76 PJ**
- **Saved CO_2 ~ 1000 kg/capita**

The CO_2 Electrofuel Project

SERC

DTU

VOLVO e.on CHEMREC

Energy to Succeed

Nýsköpunarmiðstöð Íslands

Olíudreifing

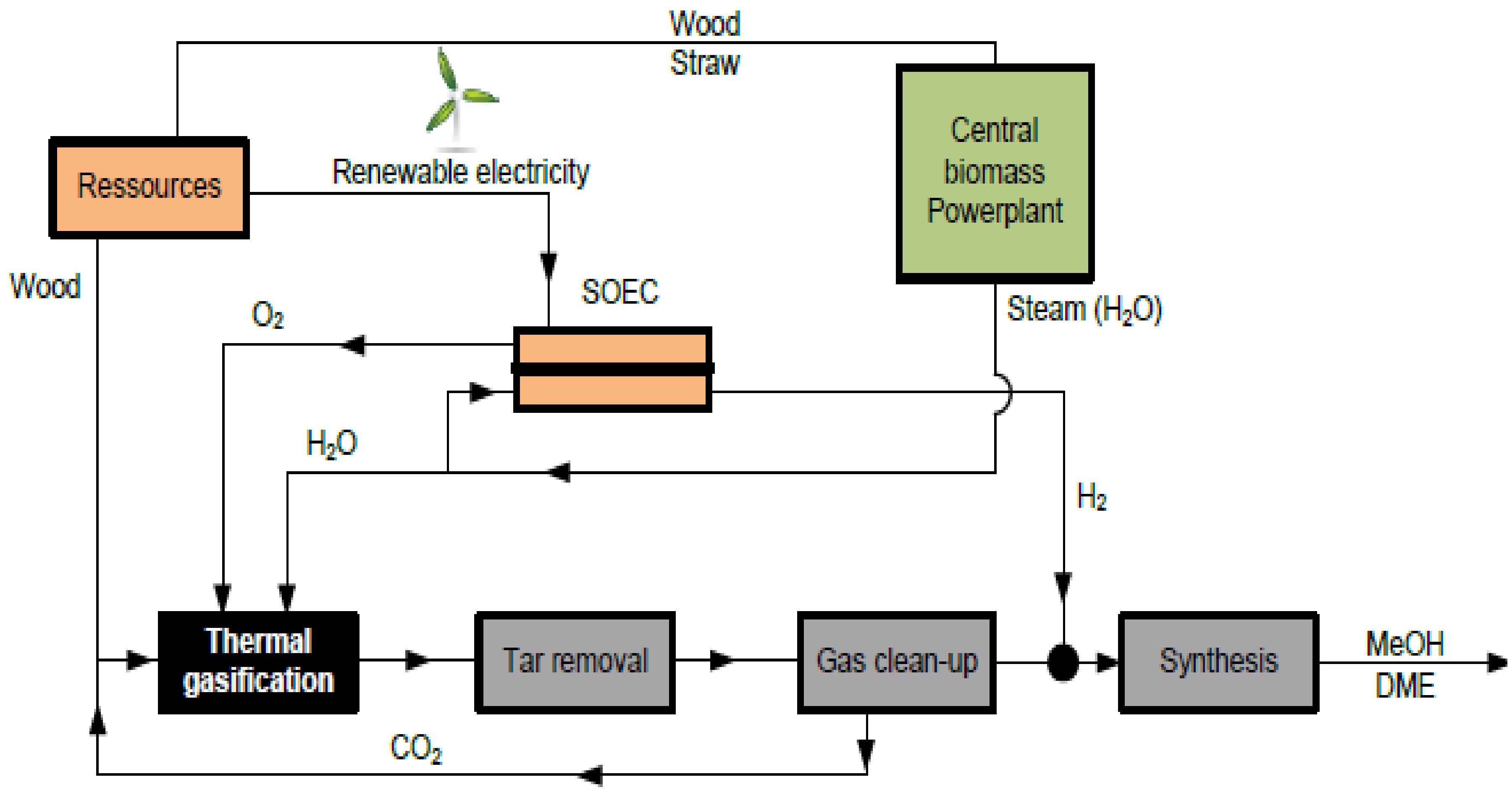
SORPA Flokkum og skilum

WÄRTSILÄ

Ea Energy Analyses HALDOR TOPSØE DTU

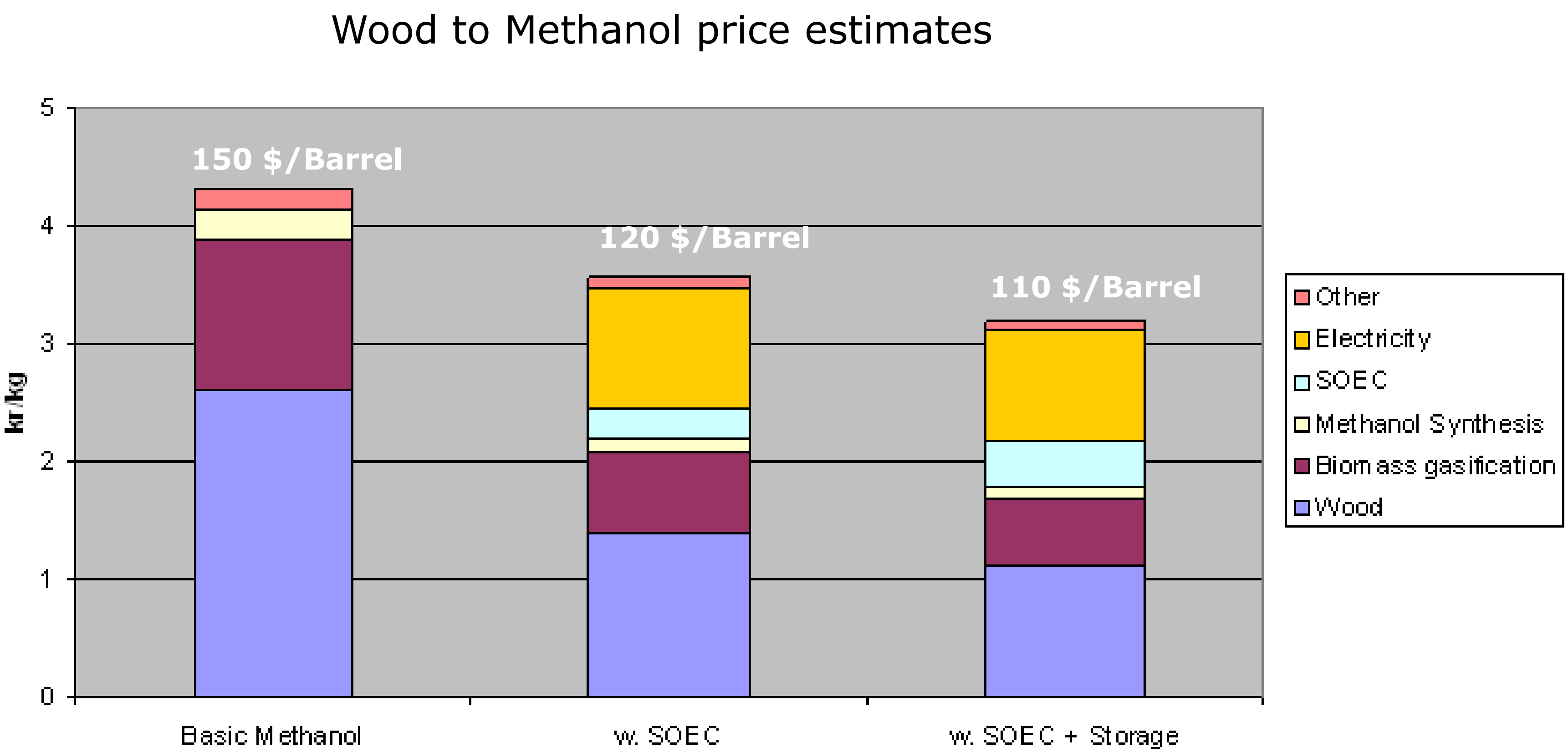
Is CO_2 electrofuels a viable and competitive technology for the Nordic countries?

GreenSynFuel Project



Some words on economics

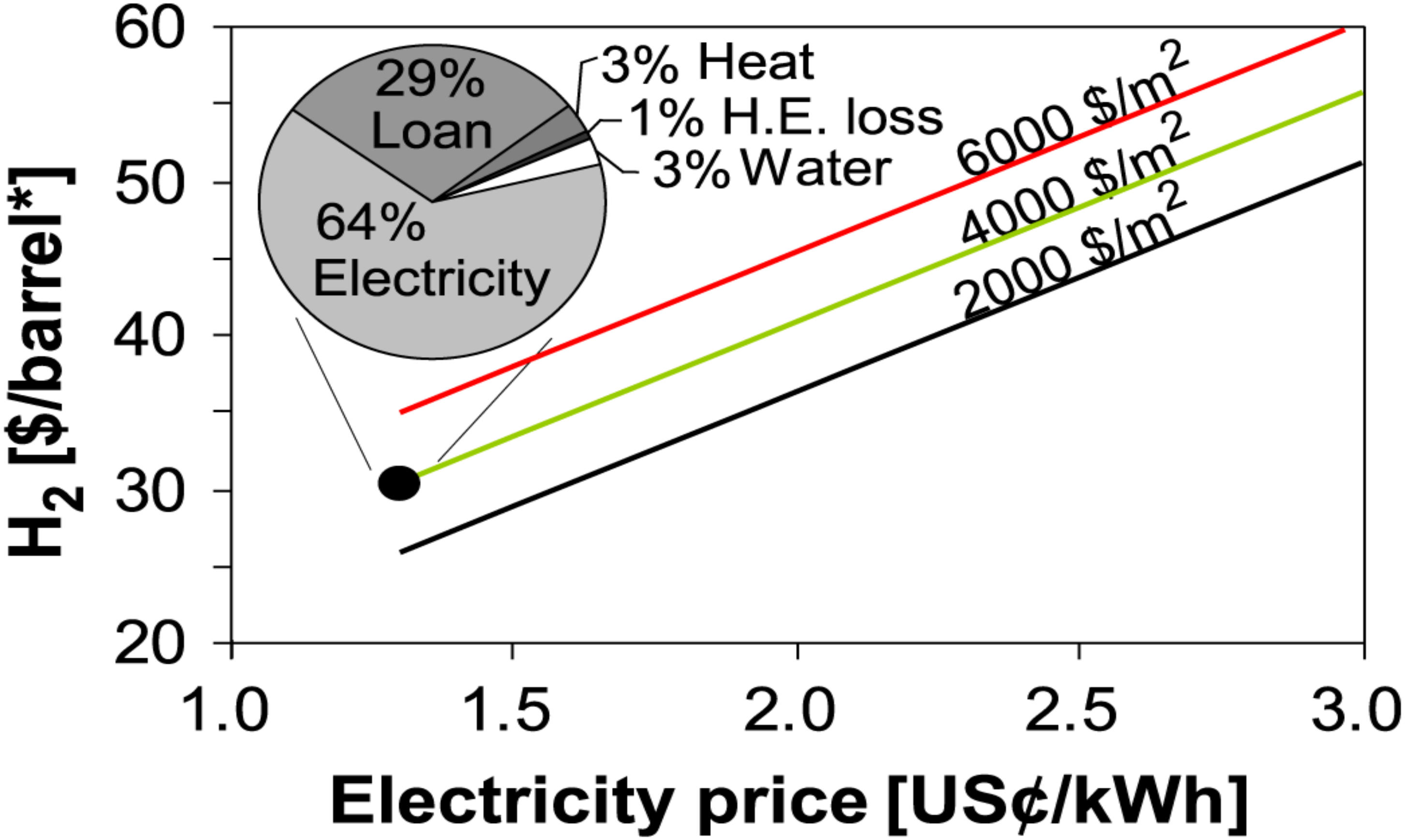
Is this (economically) viable?



Economy assumptions for H_2 production using SOEC

Electricity	1.3US¢/kWh
Heat	0.3US¢/kWh
Investment	4000 $/m^2$ cell area
Demineralised Water	2.3 $/m^3$
Cell temperature	850 ° C
Heat reservoir temperature	110 °C
Pressure	1 atm
Cell voltage	1.29 V (thermo neutral potential)
Life time	10 years.
Operating activity	50%
Interest rate	5%
Energy loss in heat exchanger	5%
H_2O inlet concentration	95% (5% H_2)
H_2O outlet concentration	5% (95% H_2)

H_2 production – economy estimation

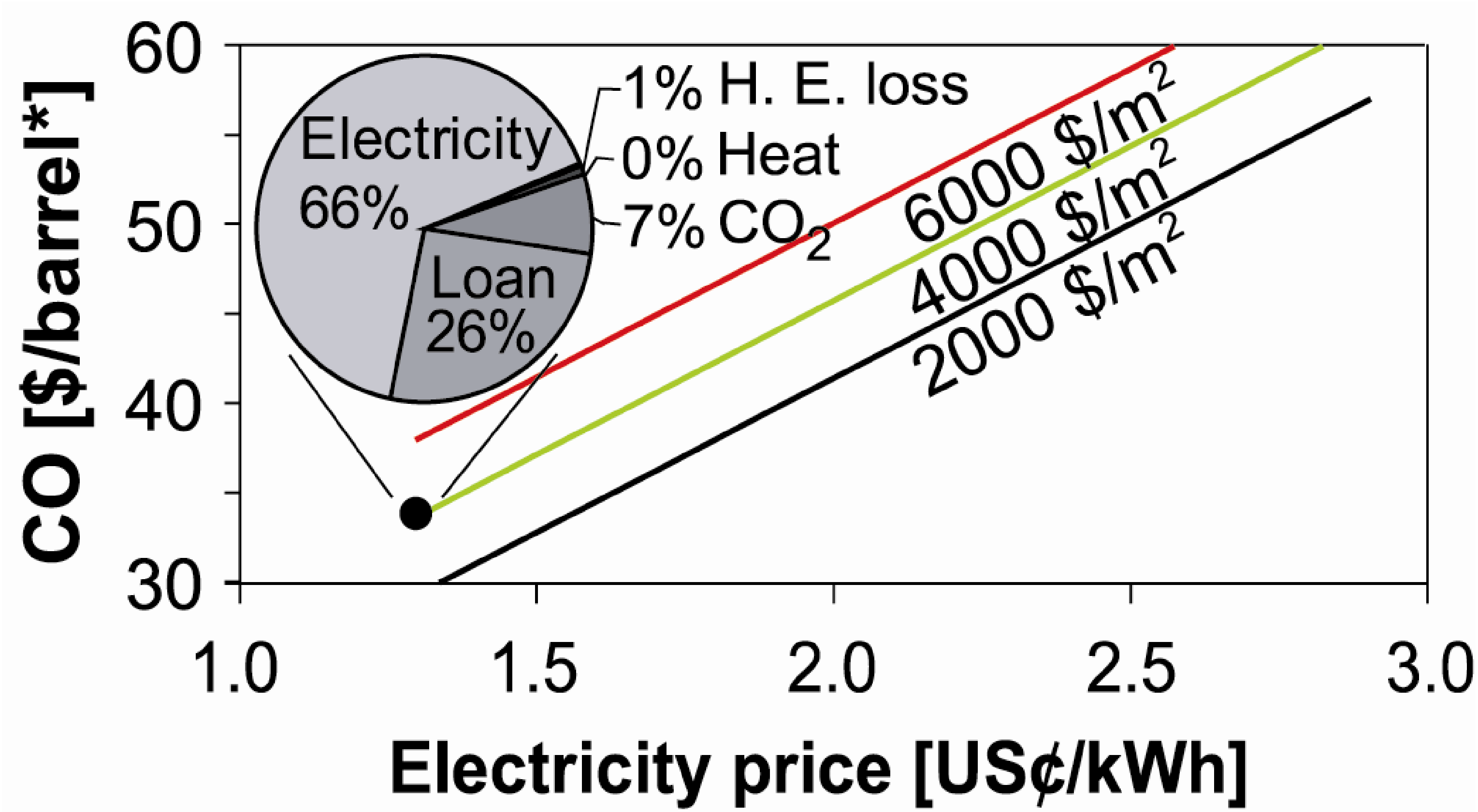


* Conversion of H_2 to equivalent crude oil price is on a pure energy content (J/kg) basis

Economy assumptions for CO production by SOEC

Electricity	1.3US¢/kWh
Heat	0.3US¢/kWh
Investment	4000 $/m^2$ cell area
CO_2	2.3 $/ton
Cell temperature	850 ° C
Heat reservoir temperature	110 °C
Pressure	1 atm
Cell voltage*	1.47 V (thermo neutral potential)
Life time	10 years.
Operating activity	50%
Interest rate	5%
Energy loss in heat exchanger	5%
CO_2 inlet concentration	95% (5% CO)
CO_2 outlet concentration	5% (95% CO)

CO production – economy estimation



* Conversion of CO to equivalent crude oil price is on a pure energy content (J/kg) basis

Concluding remarks

The following slides are meant as contributions to the discussion about what is really important and necessary to realize in the further struggle towards affordable, renewable energy.

Problems

- **Costs, costs and costs, which have different disguises:**

- **Fabrication cost**
- **Performance/efficiency**
- **Durability**

- **Risk = reliability**

- **Annoyance and disturbance of people (noise, vibration, ugly appearance,.....)**

We have to improve it all – and it is a never ending process

Efficiency versus costs

If an energy technology is sustainable (CO_2 – neutral), constantly available and environmental friendly, then the energy efficiency is not important in itself. The energy price for the consumer is the only important factor

The SOC electrolysis – fuel cell cycle-efficiency may for the time being be only 40 %. Most of the round-trip-loss is in the fuel cell (heat "loss").

Efficiency of conversion of fossil fuel in a car ca. 25 % and in a power plant ca. 40 %

Efficiency of production of bio-ethanol??

Competitive to fossil fuel?

- **Renewable electricity (wind, solar) + SOC will not be competitive to fossil derived fuels within the foreseeable future.**
- **The free market will favor cheap coal and natural gas within the foreseeable future.**
- **Political intervention is absolutely necessary - the free market forces will not save the climate. A suitable high tax on CO_2 is one way.**
- **Liquid synfuels and SNG can affordably be fabricated from syngas derived from coal. This was previously practiced in large scale in Germany during 2. world war and in South Africa during the blockade period.**

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